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# PATENT ABSTRACTS OF JAPAN

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## (54) RARE-EARTH ELEMENT-IRON-BORON PERMANENT MAGNET AND ITS MANUFACTURE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a rare-earth element-Fe-B permanent magnet which is unisotropic and has high magnetic characteristics, and its manufacturing method.

SOLUTION: An alloy having mixed texture is manufactured through the use of a strip casting method. In the mixed texture, rich alloy phase of Fe and/or Co and/or Fe and Co which densely contains one element from among Fe, Co, Fe alloy and Co alloy is made fine particles whose diameter is at most 1  $\mu$ m, and dispersed and deposited in R<sub>2</sub>(Fe, Co)<sub>14</sub>B compound phase (R is at least one kind of rare-earth element containing Y). This alloy is mixed with an R-T alloy (T is Fe and/or Co), the melting point of which is lower than that of the above alloy and/or RT-B alloy and/or R-T-M-B alloy (M is at least one kind of element selected from among the elements of Al, Si, Ti, V, Cr, Ni, Cu, Zr, Nb, Mo, Hf, Ta, and W), ground, orientation-molded in magnetic field and sintered.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The rare earth elements, iron, and a boron system permanent magnet characterized by for a rich phase of an alloy of Fe which Fe, Co, Fe alloy, and Co alloy are [ any one ] deep, and is contained, Co, or/and Fe and Co serve as a particle with a particle size of 1 micrometer or less, and have the mixed organization which did the distributed deposit in the interior of an R<sub>2</sub> (Fe, Co)<sub>14</sub> B compound phase (one or more sorts of rare earth elements with which R contains Y).

[Claim 2] R (one or more sorts of rare earth elements with which R contains Y) is six to 15 atom %, and 70 to 92 atom % and Co The rare earth elements, iron, and a boron system permanent magnet according to claim 1 0.1 to 40 atom % and whose B are one to 10 atom %s. [ Fe ]

[Claim 3] The rare earth elements, iron, and a boron system permanent magnet according to claim 1 or 2 the direction of an easy axis of an R<sub>2</sub> (Fe, Co)<sub>14</sub> B compound phase (one or more sorts of rare earth elements with which R contains Y) carries out orientation, and is [ permanent magnet ] an anisotropic magnet.

[Claim 4] The strip casting method is used. In an R<sub>2</sub> (Fe, Co)<sub>14</sub>B compound phase (one or more sorts of rare earth elements with which R contains Y) An alloy which a rich phase of an alloy of Fe which Fe, Co, Fe alloy, and Co alloy are [ any one ] deep, and is contained, Co, or/and Fe and Co serves as a particle with a particle size of 1 micrometer or less, and has a mixed organization which did the distributed deposit is produced. this -- a R-T alloy with the melting point lower than the alloy (T is Fe and/or Co), a R-T-B alloy (T is Fe and/or Co), or/and a R-T-M-B alloy (and/or, it Co(es) T -- Fe --) M is the manufacture method of of the rare earth elements, iron, and a boron system permanent magnet which is mixed with 1 or two elements or more which were chosen from aluminum, Si, Ti, V, Cr, nickel, Cu, Zr, Nb, Mo, Hf, Ta, or W, and is characterized by grinding, orientation in a magnetic field, and sintering.

[Claim 5] A manufacture method of of a rare earth elements, iron, and a boron permanent magnet according to claim 4 that peripheral velocity of a roll is 40m/second or less more than 0.5 m / second in case the strip casting method is performed.

[Claim 6] A manufacture method of of a rare earth elements, iron, and a boron permanent magnet according to claim 4 or 5 that cooling indoor ambient pressure is one or less atmospheric pressure in case the strip casting method is performed.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to useful rare earth elements, iron and boron system permanent magnet, and its manufacture method in an electron and an electrical machinery and apparatus industrial field.

[0002]

[Description of the Prior Art] The permanent magnet which consists of R (R is the same one or more sorts of the rare earth elements containing Y and the following), Fe, Co, and B, and the rare earth magnet which uses Nd as a principal component especially as R are widely used in the field of an electron and electrical machinery and apparatus industry from the height of the magnetic properties. As a manufacturing method of rare earth magnet alloy powder, there are the dissolution grinding method and a direct reduction diffusion method. The former is the method of carrying out weighing capacity of it to a necessary presentation, melting and alloying the whole, using a metal as a raw material, grinding this, and making it into the alloy-powder end of necessary grain size. On the other hand, the latter is the method of using a rare earth oxide, Fe powder, a Fe-B alloy powder, etc. for a raw material, fully being mixed, after carrying out weighing capacity of this to a necessary presentation, and being heating these with reducing agents, such as calcium, performing the reduction reaction and diffusion reaction of an oxide simultaneously, and producing the end of an alloy powder.

[0003] Although the dissolution grinding method has the advantage that the presentation of an alloy is easily controllable, it has defects, such as that an elevated temperature and severe ambient atmosphere control are required on the occasion of the dissolution, and using a rare earth metal expensive as a raw material. Moreover, Fe of a primary phase tends to deposit at the time of casting, and the rich phase of rare earth segregates simultaneously. A direct reduction diffusion method has using a comparatively cheap rare earth oxide as a raw material, not needing a not much high temperature, and the powdered alloy obtained, and although there are advantages, such as not needing the process of coarse grinding, in case control of an alloy presentation rinses the oxide produced by the unnecessary reducing agent or the reduction after a difficult thing and a reduction diffusion reaction, it has defects, like the oxygen density of an alloy goes up. Moreover, although the rich phase of rare earth is generated around the R<sub>2</sub>Fe<sub>14</sub>B main phase on the principle of compound generation and a segregation becomes small compared with the dissolution grinding method, it is easy to oxidize simultaneously and becomes the cause of the variation in a magnet property.

[0004] In order to raise the magnetic properties of rare earth, iron, and a boron system permanent magnet generally, it is a ferromagnetic layer in a permanent magnet, and it is effective to increase the rate of the R<sub>2</sub>Fe<sub>14</sub>B phase of the main phase. however, when a presentation is brought close to R<sub>2</sub>Fe<sub>14</sub>B of the main phase by the aforementioned method, the primary phase in an alloy is big and rough -- there is a problem that the segregation of Fe or a rare earth rich phase becomes large, and grinding becomes difficult simultaneously at the time of grinding.

[0005] Two alloying methods are mentioned as a method of improving this. This is the method of making the alloy of the portion which is mainly a ferromagnetic phase in a rare earth permanent magnet, and is set to R<sub>2</sub>Fe<sub>14</sub>B of the main phase, and the alloy used as the rare earth rich phase which sintering is promoted

[ phase ], and the main phase front face is cleaned [ phase ] simultaneously, and increases coercive force independently and sintering [ mix, pulverize and ]. however, into the alloy which serves as the main phase in this method, a primary phase is big and rough -- since the segregation of Fe becomes easy to happen, it heat-treats at a suitable temperature and it is necessary to homogenize an alloy.

[0006] In order to prevent a deposit and big-and-rough-izing of Fe of big-and-rough-izing of the crystal grain which is the defect of the dissolution grinding method, and a primary phase, there is the strip casting method for using a single roll or a congruence roll and quenching the molten metal of an alloy. By this method, by adjusting suitably the rotational frequency of the roll in the case of cooling, the amount of blowouts of molten metal, and cooling indoor ambient pressure, the cooling rate of molten metal can be changed, the big and rough primary phase Fe can be lost by that cause, and the thin band of the alloy which has main phase R2 Fe14B of the homogeneous and suitable diameter of crystal grain simultaneously can be obtained.

[0007] On the other hand, there is the melt span method in the manufacturing method of an isotropic magnet. Although this is the strip casting method and a method of quenching the molten metal of an alloy using a single roll or a congruence roll similarly, a cooling rate's being amorphous very early or the thin band of the alloy of a microcrystal is obtained. If a thin band is heat-treated on suitable conditions, the R2 Fe14 B phase of the main phase will carry out crystal growth, it will come to have coercive force, and an isotropic permanent magnet will be obtained.

[0008] Moreover, the composite material of hard phases, such as Nd2 Fe14 B/Fe and Nd2 Fe14 B/Fe3 B, and a soft phase was produced by this method recently. With both these magnets, the hard phase and soft phase of a nano-scale are intermingled in an alloy, switched connection is carried out magnetically, and the demagnetization curve as if it was a single hard phase is obtained. In the demagnetization curve, these are called the exchange spring magnet in order to show the unique behavior in which magnetization carries out springback reversibly to change of an external magnetic field.

[0009]

[Problem(s) to be Solved by the Invention] In current, the thing of 50MGOe for which  $BH_{max} = 64\text{MGOe}$  of a theoretical limit is pressed is also going to be mass-produced as a result of amelioration with various anisotropy sintered magnets. However, since low R2 Fe14B of saturation magnetization is made into the main phase compared with Fe etc., the improvement of magnetic properties has also been approaching the limit. On the other hand, since the exchange spring magnet also contains a phase like high Fe and Fe3 B of saturation magnetization besides the R2 Fe14 B phase, potential magnetic properties are high, but since the alloy produced by the melt span method is heat-treated and it is manufactured, the R2 Fe14 B phase has turned to the direction where an easy axis is scattering with isotropy. it is therefore, like a sintered magnet -- it is different direction-like and the high thing of magnetic properties is not obtained. This invention offers a technical problem high rare earth elements, iron and boron permanent magnet, and the manufacture method of different direction-magnetic properties.

[0010]

[Means for Solving the Problem] this invention persons completed this invention, as a result of considering and examining various methods, in order to obtain an exchange spring magnet of an anisotropy. This invention inside an R2 (Fe, Co)14 B compound phase Namely, Fe, the rare earth elements, iron, and a boron system permanent magnet characterized by for a rich phase of an alloy of Fe which Co, Fe alloy, and Co alloy are [ any one ] deep, and is contained, Co, or/and Fe and Co serving as a particle with a particle size of 1 micrometer or less, and having the mixed organization which did the distributed deposit -- and The strip casting method is used. In an R2 (Fe, Co)14 B compound phase An alloy which a rich phase of an alloy of Fe which Fe, Co, Fe alloy, and Co alloy are [ any one or more ] deep, and is contained, Co, or/and Fe and Co serves as a particle with a particle size of 1 micrometer or less, and has a mixed organization which did the distributed deposit is produced. it -- a R-T alloy with the melting point lower than the alloy (and/or, it Co(es) T -- Fe --) below the same -- or/and, a R-T-B alloy or/and a R-T-M-B alloy (1 or two elements or more with which M was chosen from aluminum, Si, Ti, V, Cr, nickel, Cu, Zr, Nb, Mo, Hf, Ta, or W --) Below, it mixes and they are being the same, and grinding, orientation in a magnetic field and a thing

that makes a summary a manufacture method of of the rare earth elements, iron, and a boron system permanent magnet characterized by sintering.

[0011]

[Embodiment of the Invention] The permanent magnet of this invention makes the main phase alloy which has the R<sub>214</sub>(Fe, Co) B compound phase which is the particle size of 2–10 micrometers dotted with the software phase of a nano-scale by a suitable presentation and the strip casting method of conditions, mixes this with the assistant alloy which contains a rare earth rich phase with the low melting point, and are grinding and a thing which orientation[ in a magnetic field ]–fabricates, sinters and is manufactured. the feature of this invention -- \*\* -- it is the strip cast method using the alloy of a suitable presentation, and quenching conditions, and the thin band alloy with which the rich phase of Fe in which Fe, Co, Fe alloy, and Co alloy are contain 90% of the weight or more, or/and the rich phase (it is call a T' rich phase below) of Co serve as a particle of a nano-scale, and consists of an R<sub>214</sub>(Fe, Co) B compound phase with a particle size of 2–10 micrometers which distributes inside minutely and exists in it be obtain.

\*\* The obtained thin band alloy is used as the main phase alloy, and the sintered magnet of an anisotropy is obtained more in this by the assistant alloy of the low melting point, mixing, grinding, and two so-called alloying methods that orientation[ in a magnetic field ]–fabricate and are sintered.

\*\* Simultaneously, when a thin band alloy contains the software phase of a nano-scale in a hard phase, the high hard magnetism phase of coercive force and a T' rich phase with elasticity magnetism carry out switched connection, and realize anisotropy rare earth elements, iron, and a boron system permanent magnet alloy with high saturation magnetization, maintaining the coercive force which a hard magnetism phase has.

[0012] Below, this is explained further in full detail. First, it melts beforehand and the main phase alloy is produced. R makes the presentation of an alloy five to 14 atom %. When main phase R<sub>214</sub>(Fe, Co) B for maintaining coercive force if R is under pentatomic % runs short and 14 atom % is exceeded, the rate of main phase R<sub>214</sub>(Fe, Co) B increases, and a T' rich phase stops already depositing. B is taken as three to 20 atom %. If the deposit of a detailed T' rich phase will stop being able to happen easily, and it will become a big and rough sludge, if B is under 3 atom %, and 20 atom % is exceeded, a paramagnetism phase will deposit and coercive force will be reduced. Fe or/and Co are taken as 65 to 93 atom %. Although the rate of the T' rich phase in main phase R<sub>214</sub>(Fe, Co) B will become large and will enlarge the saturation magnetization of a permanent magnet if the deposit of a paramagnetism phase will increase, coercive force will be reduced, if this is under 65 atom %, and 93 atom % is exceeded, the melting point of an alloy is got and it becomes a big and rough sludge simultaneously.

[0013] Subsequently, the molten metal of the produced main phase alloy is quenched by the strip casting method by the single rolling method or the congruence rolling method, and a thin band is produced. Peripheral velocity of a roll is carried out in 0.5–40m/second. Switched connection of the big and rough software phase which the cooling rate was lacking when peripheral velocity was under 0.5 m / second, the T' rich phase of a nano-scale did not deposit, but deposited as a big and rough primary phase, and deposited in this way is not carried out to a hard phase any longer. On the other hand, if peripheral velocity exceeds a second in 40m /, although a detailed software phase deposits, even if it cannot grind it so that the diameter of crystal grain of the R<sub>214</sub>(Fe, Co) B phase which is a hard phase may also become small and may become a single domain at a next grinding process, but it carries out orientation shaping in a magnetic field, it will not serve as an anisotropic magnet.

[0014] An assistant alloy is melted. As an assistant alloy, what has the melting point lower than the main phase alloy is good, and considers as a R–T alloy, a R–T–B alloy, or/and a R–T–M–B alloy. The melting point becomes high, so that in [ any ] an assistant alloy, as for the melting point, it becomes low, so that the content of R becomes large, and the content of T becomes large. If B has many additions, a paramagnetism phase will deposit and it will drop magnetic properties. Although M makes the coercive force of the sintered permanent magnet increase, saturation magnetization is decreased, in order to make the element and alloy in the main phase and to reduce the rate of main phase R<sub>214</sub>(Fe, Co) B, if it puts in too much. therefore -- a R–T alloy -- R -- 12 to 80 atom %, Remainder T, and a R–T–B alloy -- R --

below 10 atom %, with Remainder T and a R-T-M-B alloy, R uses M to 12 to 80 atom % below 10 atom %, and B uses 12 to 80 atom %, and B as Remainder T below pentatomic %. In order to use the cast alloy as it is and to obtain a uniform alloy with more few segregations, the strip casting method is used for an assistant alloy, and it is good also as a quenching thin band.

[0015] Subsequently, the main phase alloy and an assistant alloy are ground. Grinding is performed in inert atmospheres, such as N<sub>2</sub> and Ar. You may make it easy to grind by performing a hydrogen treating and dehydrogenation processing beforehand, when a presentation is hard to grind these alloys. Hydrogenation conditions are 0–50 degrees C and H<sub>2</sub>. It is 1.5 to \*\* 3 atmospheric pressure, and 0.5 – 10 hours, and dehydrogenation conditions are 0.5 – 10 hours among 200 – 600 \*\* and a vacuum. Coarse grinding of the main phase alloy and the assistant alloy is first carried out using a jaw crusher etc. The main phase alloy and assistant alloy which carried out coarse grinding are mixed to a predetermined presentation. At this time, 70 to 92 atom % and Co It mixes so that 0.1 to 40 atom % and B may set it one to 10 atom % and the remainder may be set to M. [ a presentation ] [ R ] [ six to 15 atom %, and Fe ] each component of a presentation — this — if out of range, sintering is not fully performed, or residual magnetization is dropped. A mixed alloy is pulverized with a ball mill, a jet mill, etc. The R<sub>2</sub> 14 (Fe, Co) B phase in the main phase alloy grinds a mixed alloy in the range of 1–10 micrometers of the particle size used as a single domain.

[0016] Next, orientation shaping in a magnetic field of the pulverized mixed alloy is carried out. The conditions of orientation shaping in a magnetic field are a magnetic field 5 – 15kOe, and compacting pressure 300 – 2,000 kgf/cm<sup>2</sup>. It is desirable.

[0017] Subsequently, the green compact which carried out orientation shaping in a magnetic field is sintered. Sintering conditions are made into the sintering temperature 1,050 – 1,200 \*\* in inert atmospheres, such as N<sub>2</sub> and Ar, or a vacuum. If sintering temperature is under 1,050 \*\*, the density of a sintered compact will not go up enough, but if coercive force is also low and exceeds 1,200 \*\* simultaneously, R<sub>2</sub> 14 (Fe, Co) B phase will carry out grain growth greatly, and coercive force will fall.

[0018]

[Example] Next, although an example is given and the gestalt of operation of this invention is explained concretely, this invention is not limited to these.

(Examples 1–3) The alloy was beforehand produced with the RF fusion furnace so that it might become the presentation of a table 1. This alloy was put into the quartz tube which has a with a width-of-face length [ 35mm length of 1mm ] slit, and carried out high-frequency heating about 1kg at a time to ejection and a pars basilaris ossis occipitalis, respectively. Heating was performed in Ar ambient atmosphere of pressure 26cmHg. In the place where the temperature of molten metal became 1,350 \*\*, pressurized the surface of hot water by Ar gas, the copper roll side currently rotated with the roll peripheral velocity of 10m/second was made to spout molten metal from a height of 2mm, and the quenching thin band was produced. The produced thin band is to the interior of Nd<sub>2</sub> Fe<sub>14</sub> B phase with a particle size of 2–5 micrometers, when it is width of face of 10–15mm, and 50 to 100 micrometer thickness and being observed by EPMA. It had the organization where the detailed T' rich phase of 0.5 micrometers or less deposits. Hydrogenation and dehydrogenation processing were performed on this thin band. Performing hydrogenation conditions in 20 degrees C, hydrogen pressure 2 atmospheric pressure, and 2 hours, dehydrogenation conditions are 4 hours among 500 \*\* and a vacuum. A jaw crusher and BURAUMMIRU are used for this thin band, and it is mean particle diameter 500. It considered as the main phase alloy-powder end of mum. Subsequently, mixed fusion of the element of the presentation shown in a table 2 is carried out at the rate of a table, an assistant alloy is produced, a jaw crusher and BURAUMMIRU are used, and it is mean particle diameter 400 about this. Coarse grinding was carried out to mum and the end of an assistant alloy powder was produced. After mixing 88% of the weight in the end of the main phase alloy powder, using V blender as the end of a remainder assistant alloy powder, this was pulverized in mean particle diameter of 3 micrometers using the jet mill. It is the powder pulverized and obtained Magnetic field 10kOe and compacting pressure 500 kgf/cm<sup>2</sup> Orientation shaping in a magnetic field was carried out. The green compact fabricated and obtained was sintered by 1,120 \*\* in the vacuum for 2 hours, and the anisotropy permanent magnet was obtained. The magnetic properties of the obtained magnet are shown in a table 3.



[0019]

[A table 1]

| 元 素   |   | Nd   | Fe   | Co | B   |
|-------|---|------|------|----|-----|
| 実 施 例 | 1 | 10.5 | 83   | 1  | 5.5 |
|       | 2 | 9    | 84   | 1  | 6   |
|       | 3 | 8.5  | 83.5 | 1  | 7   |

単位は原子%

[0020]

[A table 2]

| 元素 | Nd | Dy | Fe | Co | B | Cu | Al |
|----|----|----|----|----|---|----|----|
|    | 45 | 13 | 15 | 23 | 1 | 2  | 1  |

単位は原子%

[0021]

[A table 3]

| 磁 気 特 性 |   | 保磁力 (kOe) | 残留磁化 (kG) |
|---------|---|-----------|-----------|
| 実 施 例   | 1 | 3.1       | 13.1      |
|         | 2 | 2.5       | 13.5      |
|         | 3 | 2.9       | 13.2      |

[0022] (Examples 1-3 of a comparison) The example 3 of a comparison of an example 2 carried out the RF dissolution, as the example 2 of a comparison of an example 1 became the same with the presentation of the table 1 of an example 3, respectively, the example 1 of a comparison cast the alloy presentation, and the alloy of the examples 1-3 of a comparison was produced. When these alloys were measured by EPMA, it is mean particle diameter 100. It is mean particle diameter 200 in the Nd<sub>2</sub> Fe<sub>14</sub> B phase of mum. It had the organization where the T' rich phase of mum deposits. Coarse grinding of the alloy was carried out using a jaw crusher and BURAUMMIRU like the example. The sintered magnet was produced like the example using this end of an alloy powder. The magnetic properties of these magnets are shown in a table 4.

[0023]

[A table 4]

| 磁 気 特 性 |   | 保磁力 (kOe) | 残留磁化 (kG) |
|---------|---|-----------|-----------|
| 比 較 例   | 1 | 0.2       | 6.5       |
|         | 2 | 0.1       | 5.5       |
|         | 3 | 0.2       | 6.3       |

[0024]

[Effect of the Invention] According to this invention, rare earth elements, iron, and a boron system anisotropy permanent magnet alloy with high saturation magnetization can be obtained, a hard phase and a software phase carrying out switched connection inside a hard phase, and maintaining the coercive force of a hard phase inside, when the detailed software phase is distributing.

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(54)【発明の名称】 希土類元素・鉄・ボロン系永久磁石およびその製造方法

(57)【要約】 (修正有)

【課題】 異方性で磁気特性が高い希土類元素・鉄・ボロン永久磁石とその製造方法の提供。

【解決手段】 ストリップキャスティング法を用いて、 $R_2(Fe, Co)_{14}B$ 化合物相(RはYを含む希土類元素の1種以上)中に、Fe、Co、Fe合金、Co合金のいずれか1つを濃く含有するFeまたは／およびCoまたは／およびFeとCoの合金のリッチ相が粒径1 $\mu$ m以下の微粒子となって分散析出した混合組織を有する合金を作製し、これをその合金より融点の低いR-T合金(TはFeおよび／またはCo)または／およびR-T-B合金または／およびR-T-M-B合金(MはAl, Si, Ti, V, Cr, Ni, Cu, Zr, Nb, Mo, Hf, Ta, Wの元素のいずれかより選ばれた1以上の元素)と混合し、粉碎、磁場中配向成形、焼結する希土類元素・鉄・ボロン系永久磁石の製造方法。

(2)

## 【特許請求の範囲】

【請求項1】  $R_2(Fe, Co)_{14}B$ 化合物相(RはYを含む希土類元素の1種以上)内部に、Fe、Co、Fe合金、Co合金のいずれか1つを濃く含有するFeまたは/およびCoまたは/およびFeとCoの合金のリッチ相が粒径1 $\mu m$ 以下の微粒子となって分散析出した混合組織を持つことを特徴とする希土類元素・鉄・ボロン系永久磁石。

【請求項2】 R(RはYを含む希土類元素の1種以上)が6~15原子%、Feが70~92原子%、Coが0.1~40原子%、Bが1~10原子%である請求項1に記載の希土類元素・鉄・ボロン系永久磁石。

【請求項3】  $R_2(Fe, Co)_{14}B$ 化合物相(RはYを含む希土類元素の1種以上)の磁化容易軸方向が配向し、異方性磁石である請求項1または請求項2に記載の希土類元素・鉄・ボロン系永久磁石。

【請求項4】 ストリップキャスト法を用いて、 $R_2(Fe, Co)_{14}B$ 化合物相(RはYを含む希土類元素の1種以上)中に、Fe、Co、Fe合金、Co合金のいずれか1つを濃く含有するFeまたは/およびCoまたは/およびFeとCoの合金のリッチ相が粒径1 $\mu m$ 以下の微粒子となって分散析出した混合組織を有する合金を作製し、これをその合金より融点の低いR-T合金(TはFeおよび/またはCo)または/およびR-T-B合金(TはFeおよび/またはCo)または/およびR-T-M-B合金(TはFeおよび/またはCo、MはAl、Si、Ti、V、Cr、Ni、Cu、Zr、Nb、Mo、Hf、Ta、Wのいずれかより選ばれた1または2つ以上の元素)と混合し、粉碎、磁場中配向、焼結することを特徴とする希土類元素・鉄・ボロン系永久磁石の製造方法。

【請求項5】 ストリップキャスト法を行う際にロールの周速度が0.5 m/秒以上40m/秒以下である請求項4に記載の希土類元素・鉄・ボロン系永久磁石の製造方法。

【請求項6】 ストリップキャスト法を行う際に冷却室内雰囲気圧が1気圧以下である請求項4または請求項5に記載の希土類元素・鉄・ボロン系永久磁石の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、電子・電気機器産業分野で有用な、希土類元素・鉄・ボロン系永久磁石およびその製造方法に関するものである。

## 【0002】

【従来の技術】R(RはYを含む希土類元素の1種以上、以下同じ)、Fe、Co、Bからなる永久磁石、特にRとしてNdを主成分とする希土類磁石は、その磁気特性の高さから電子・電気機器産業の分野において、広く利用されている。希土類磁石合金粉末の製造法とし

2

て、熔解粉碎法と直接還元拡散法がある。前者は、原料として金属を用い、それを所要の組成に秤量し、全体を熔解して合金化し、これを粉碎し所要粒度の合金粉末とする方法である。一方後者は、原料に希土類酸化物、Fe粉、Fe-B合金粉等を使用し、これを所要の組成に秤量したのち十分に混合し、これらをCa等還元剤と共に加熱することで、酸化物の還元反応および拡散反応を同時に行い、合金粉末を作製する方法である。

【0003】熔解粉碎法は、合金の組成を容易に制御できるという利点を持っているが、熔解に際して高温と厳しい雰囲気制御が要求されること、原料として高価な希土類金属を用いること等の欠点がある。また、鑄造時に初晶のFeが析出しやすく、同時に希土類のリッチ相が偏析する。直接還元拡散法は、比較的安価な希土類酸化物を原料として用いること、あまり高い温度を必要としないこと、得られる合金が粉末状態で粗粉碎の工程を必要としないこと等の利点があるが、合金組成の制御が難しいこと、還元拡散反応後の不要な還元剤あるいは還元により生じた酸化物を水洗する際に、合金の酸素濃度が上昇してしまうこと等の欠点がある。また化合物生成の原理上、 $R_2Fe_{14}B$ 主相の周囲に希土類のリッチ相が生成され、熔解粉碎法に比べ偏析は小さくなるが、同時に酸化しやすく、磁石特性のバラツキの原因となる。

【0004】一般に希土類・鉄・ボロン系永久磁石の磁気特性を向上させるためには、永久磁石中の強磁性層であり主相の $R_2Fe_{14}B$ 相の割合を増やすことが有効である。しかし、前記の方法では、組成を主相の $R_2Fe_{14}B$ に近づけると、合金中の初晶の粗大Feや希土類リッチ相の偏析が大きくなり、同時に粉碎時に粉碎が困難になるという問題がある。

【0005】これを改善する方法として、二合金法が挙げられる。これは、希土類永久磁石中で主に強磁性相であり主相の $R_2Fe_{14}B$ となる部分の合金と、焼結を促進し同時に主相表面をクリーニングし保磁力を増大させる希土類リッチ相となる合金を別々に作り、混合、粉碎、焼結する方法である。ただし、この方法において主相となる合金には、初晶の粗大Feの偏析が起こりやすくなるので、適当な温度で熱処理し、合金を均質化してやるが必要になる。

【0006】熔解粉碎法の欠点である結晶粒の粗大化、初晶のFeの析出および粗大化を防止するために、合金の熔湯を単ロールまたは双ロールを用いて急冷するストリップキャスト法がある。この方法では、冷却の際のロールの回転数、熔湯の噴出量および冷却室内雰囲気圧を適当に調節することによって、熔湯の冷却速度を変えることができ、それにより粗大な初晶Feをなくし、同時に均質で適当な結晶粒径の主相 $R_2Fe_{14}B$ をもつ合金の薄帯を得ることが出来る。

【0007】一方、等方性磁石の製造法では、メルトスパン法がある。これは、ストリップキャスト法と

(3)

3

同様に合金の熔湯を単ロールまたは双ロールを用いて急冷する方法であるが、冷却速度が非常に早く、アモルファスあるいは微結晶の合金の薄帯が得られる。薄帯を適当な条件で熱処理すると、主相の $R_2Fe_{14}B$ 相が結晶成長し、保磁力を持つようになり、等方性の永久磁石が得られる。

【0008】また、最近この方法により $Nd_2Fe_{14}B/Fe$ 、 $Nd_2Fe_{14}B/Fe_3B$ 等のハード相とソフト相の複合材料が作製された。これらの磁石では、合金中に共にナノスケールのハード相とソフト相が混在し、磁氣的に交換結合して、あたかも単一のハード相であるかのような減磁曲線が得られている。これらは、減磁曲線において、磁化が外部磁界の変化に対し可逆的にスプリングバックする特異な挙動を示すため、交換スプリング磁石と呼ばれている。

【0009】

【発明が解決しようとする課題】現在では、異方性焼結磁石は様々な改良の結果、理論的限界の $BH_{max} = 64 \text{ MGOe}$ に迫る、 $50 \text{ MGOe}$ のものも量産されようとしている。しかし、 $Fe$ などに比べて飽和磁化の低い $R_2Fe_{14}B$ を主相としているため、磁気特性の改善も限界に近づいてきている。一方、交換スプリング磁石は、 $R_2Fe_{14}B$ 相の他に飽和磁化の高い $Fe$ や $Fe_3B$ の様な相も含んでいるため、潜在的な磁気特性は高いが、メルトスパン法で作製された合金を熱処理して製造されるので、 $R_2Fe_{14}B$ 相は等方性で磁化容易軸がバラバラの方向を向いている。したがって、焼結磁石のような異方的で磁気特性の高いものは得られていない。本発明は、異方的磁気特性の高い希土類元素・鉄・ボロン永久磁石とその製造方法の提供を課題とするものである。

【0010】

【課題を解決するための手段】本発明者らは、異方性の交換スプリング磁石を得るために様々な方法を考察、検討した結果、本発明を完成させた。すなわち本発明は、 $R_2(Fe, Co)_{14}B$ 化合物相内部に、 $Fe$ 、 $Co$ 、 $Fe$ 合金、 $Co$ 合金のいずれか1つを濃く含有する $Fe$ または/および $Co$ または/および $Fe$ と $Co$ の合金のリッチ相が粒径 $1 \mu m$ 以下の微粒子となって分散析出した混合組織を持つことを特徴とする希土類元素・鉄・ボロン系永久磁石、および、ストリップキャスト法を用いて、 $R_2(Fe, Co)_{14}B$ 化合物相中に、 $Fe$ 、 $Co$ 、 $Fe$ 合金、 $Co$ 合金のいずれか1つ以上を濃く含有する $Fe$ または/および $Co$ または/および $Fe$ と $Co$ の合金のリッチ相が粒径 $1 \mu m$ 以下の微粒子となって分散析出した混合組織を有する合金を作製し、それをその合金より融点の低い $R-T$ 合金( $T$ は $Fe$ および/または $Co$ 、以下同じ)または/および $R-T-B$ 合金または/および $R-T-M-B$ 合金( $M$ は $Al$ 、 $Si$ 、 $Ti$ 、 $V$ 、 $Cr$ 、 $Ni$ 、 $Cu$ 、 $Zr$ 、 $Nb$ 、 $Mo$ 、 $Hf$ 、 $Ta$ 、 $W$ のいずれかより選ばれた1または2つ以上の元

4

素、以下同じ)と混合し、粉碎、磁場中配向、焼結することを特徴とする希土類元素・鉄・ボロン系永久磁石の製造方法を要旨とするものである。

【0011】

【発明の実施の形態】本発明の永久磁石は適当な組成、条件のストリップキャスト法により、ナノスケールのソフト相が点在する粒径 $2 \sim 10 \mu m$ の $R_2(Fe, Co)_{14}B$ 化合物相をもつ主相合金を作り、これを低融点で希土類リッチ相を含む助剤合金と混合し、粉碎、磁場中配向成形、焼結して製造されるものである。本発明の特徴は、

①適当な組成の合金、急冷条件を用いたストリップキャスト法で、 $Fe$ 、 $Co$ 、 $Fe$ 合金、 $Co$ 合金が90重量%以上含まれる $Fe$ のリッチ相または/および $Co$ のリッチ相(以下 $T'$ リッチ相と呼ぶ)が、ナノスケールの微粒子となって内部に微細に分散して存在している粒径 $2 \sim 10 \mu m$ の $R_2(Fe, Co)_{14}B$ 化合物相からなる薄帯合金が得られる。

②得られた薄帯合金を主相合金とし、これをより低融点の助剤合金と混合、粉碎、磁場中配向成形、焼結するいわゆる二合金法により、異方性の焼結磁石が得られる。

③同時に、薄帯合金がナノスケールのソフト相をハード相中に含むことにより、保磁力の高い硬質磁性相と、軟質磁性を持つ $T'$ リッチ相が交換結合し、硬質磁性相の持つ保磁力を維持しながら、高い飽和磁化を持つ異方性希土類元素・鉄・ボロン系永久磁石合金を実現するものである。

【0012】以下に、これをさらに詳述する。まず主相合金を予め熔解して作製する。合金の組成は、 $R$ は5～14原子%とする。 $R$ が5原子%未満だと、保磁力を維持するための主相 $R_2(Fe, Co)_{14}B$ が不足し、14原子%を超えると、主相 $R_2(Fe, Co)_{14}B$ の割合が増え、もはや $T'$ リッチ相が析出しなくなる。 $B$ は3～20原子%とする。 $B$ が3原子%未満だと微細な $T'$ リッチ相の析出が起こりにくくなり、粗大な析出物となり、20原子%を超えると常磁性相が析出し、保磁力を低下させる。 $Fe$ または/および $Co$ は、65～93原子%とする。これが、65原子%未満だと常磁性相の析出が多くなり保磁力を低下させ、93原子%を超えると、主相 $R_2(Fe, Co)_{14}B$ 中の $T'$ リッチ相の割合が大きくなり、永久磁石の飽和磁化を大きくするが、合金の融点をあげ同時に粗大な析出物となる。

【0013】次いで作製した主相合金の熔湯を単ロール法あるいは双ロール法等によるストリップキャスト法により急冷して薄帯を作製する。ロールの周速度は、 $0.5 \sim 40 \text{ m/秒}$ とする。周速度が $0.5 \text{ m/秒}$ 未満だと冷却速度が足りず、ナノスケールの $T'$ リッチ相が析出せず、粗大な初晶として析出してしまい、こうして析出した粗大なソフト相はもはやハード相と交換結合しない。一方周速度が $40 \text{ m/秒}$ を超えると、微細なソフト相

(4)

5

は析出するが、ハード相である $R_2$  (Fe, Co) $_{14}B$ 相の結晶粒径も小さくなり、後の粉碎工程で単磁区になるように粉碎できず、磁場中配向成形しても、異方性磁石とならない。

【0014】助剤合金を熔解する。助剤合金としては、主相合金より融点の低いものがよく、R-T合金または／およびR-T-B合金または／およびR-T-M-B合金とする。いずれの助剤合金の場合も、Rの含有量が大きくなるほど融点は低くなり、Tの含有量が大きくなるほど融点は高くなる。Bは添加量が多いと、常磁性相が析出し磁気特性を落とす。Mは焼結した永久磁石の保磁力を増加させるが、入れ過ぎると主相中の元素と合金を作り、主相 $R_2$  (Fe, Co) $_{14}B$ の割合を減らすため、飽和磁化を減少させる。したがってR-T合金ではRは12～80原子%、残部T、R-T-B合金ではRは12～80原子%、Bは10原子%以下、残部T、R-T-M-B合金ではRは12～80原子%、Bは10原子%以下、Mは5原子%以下、残部Tとする。助剤合金は、鑄造した合金をそのまま用いても良いし、より偏析の少ない均一な合金を得るために、ストリップキャスティング法を用いて、急冷薄帯としても良い。

【0015】次いで主相合金および助剤合金を粉碎する。粉碎は、 $N_2$ 、Ar等の不活性雰囲気中で行う。組成により、これらの合金が粉碎しにくい場合、予め水素化処理および脱水素化処理を行って、粉碎をしやすくしてもよい。水素化条件は、0～50℃、 $H_2$ 圧1.5～3気圧、0.5～10時間で、脱水素化条件は、200～600℃、真空中、0.5～10時間である。まず主相合金および助剤合金をジョークラッシャー等を用いて粗粉碎する。粗粉碎した主相合金および助剤合金を所定の組成に混合する。このとき組成が、Rが6～15原子%、Feが70～92原子%、Coが0.1～40原子%、Bが1～10原子%、残部がMとなるように混合する。組成の各成分がこの範囲外では焼結が十分に行われなかったり、残留磁化を落としたりする。混合合金をボールミル、ジェットミル等で微粉碎する。混合合金は主相合金中の $R_2$  (Fe, Co) $_{14}B$ 相が単磁区となる粒径の1～10 $\mu m$ の範囲に粉碎する。

【0016】次に微粉碎した混合合金を磁場中配向成形する。磁場中配向成形の条件は、磁場5～15kOe、成

6

\* 形圧力300～2,000 kgf/cm<sup>2</sup>が好ましい。

【0017】次いで磁場中配向成形した圧粉体を焼結する。焼結条件は、 $N_2$ 、Ar等の不活性雰囲気中または真空中で、焼結温度1,050～1,200℃とする。焼結温度が1,050℃未満だと、焼結体の密度が十分上がらず、同時に保磁力も低く、1,200℃を超えると、 $R_2$  (Fe, Co) $_{14}B$ 相が大きく粒成長し、保磁力が下がる。

【0018】

【実施例】次に本発明の実施の形態を実施例を挙げて具体的に説明するが、本発明はこれらに限定されるものではない。

(実施例1～3)表1の組成になるように、合金を高周波溶解炉にて予め作製した。この合金をそれぞれ、約1kgずつ取り出し、底部に幅1mm長さ35mmのスリットを有する石英管にいれ、高周波加熱した。加熱は、圧力26cmHgのAr雰囲気中で行った。熔湯の温度が1,350℃になったところで、湯面をArガスにより加圧して、ロール周速度10m/秒にて回転している銅ロール面に2mmの高さから熔湯を噴出させて、急冷薄帯を作製した。作製した薄帯は、幅10～15mm、厚さ50～100 $\mu m$ であり、EPMAで観察したところ、粒径2～5 $\mu m$ のNd<sub>2</sub>Fe<sub>14</sub>B相内部に0.5 $\mu m$ 以下の微細なT'リッチ相が析出している組織を有していた。この薄帯に水素化、脱水素化処理を行った。水素化条件は20℃、水素圧2気圧、2時間で行い、脱水素化条件は、500℃、真空中、4時間である。この薄帯をジョークラッシャー、ブラウンミルを用いて、平均粒径500 $\mu m$ の主相合金粉末とした。次いで表2に示す組成の元素を表の割合に混合熔融して助剤合金を作製し、ジョークラッシャー、ブラウンミルを用いてこれを平均粒径400 $\mu m$ に粗粉碎し助剤合金粉末を作製した。主相合金粉末88重量%、残部助剤合金粉末として、Vブレンダーを用いて混合した後、ジェットミルを用いてこれを平均粒径3 $\mu m$ に微粉碎した。微粉碎して得た粉末を磁場10kOe、成形圧力500 kgf/cm<sup>2</sup>で磁場中配向成形した。成形して得られた圧粉体を真空中で1,120℃で2時間焼結して、異方性永久磁石が得られた。得られた磁石の磁気特性を表3に示す。

【0019】

【表1】

| 元 素   |   | Nd   | Fe   | Co | B   |
|-------|---|------|------|----|-----|
| 実 施 例 | 1 | 10.5 | 83   | 1  | 5.5 |
|       | 2 | 9    | 84   | 1  | 6   |
|       | 3 | 8.5  | 83.5 | 1  | 7   |

単位は原子%

【0020】

【表2】

(5)

8

| 元素 | Nd | Dy | Fe | Co | B | Cu | Al |
|----|----|----|----|----|---|----|----|
|    | 45 | 13 | 15 | 23 | 1 | 2  | 1  |

【0021】

【表3】

単位は原子%

| 磁気特性 | 保磁力 (kOe) | 残留磁化 (kG) |
|------|-----------|-----------|
| 実施例  | 1         | 3.1       |
|      | 2         | 2.5       |
|      | 3         | 2.9       |

【0022】（比較例1～3）合金組成を比較例1は実施例1の、比較例2は実施例2の、比較例3は実施例3の表1の組成とそれぞれ同じになるようにして、高周波熔解して鑄造し、比較例1～3の合金を作製した。これらの合金をEPMAで測定したところ、平均粒径100  $\mu$ mのNd<sub>2</sub>Fe<sub>14</sub>B相とともに平均粒径200  $\mu$ mのT'リッチ相が析出している組織を有していた。その合金を

実施例と同様にジョークラッシャー、ブラウンミルを用いて粗粉碎した。この合金粉末を用いて、実施例と同様に焼結磁石を作製した。これらの磁石の磁気特性を表4に示す。

【0023】

【表4】

| 磁気特性 | 保磁力 (kOe) | 残留磁化 (kG) |
|------|-----------|-----------|
| 比較例  | 1         | 0.2       |
|      | 2         | 0.1       |
|      | 3         | 0.2       |

【0024】

【発明の効果】本発明によれば、ハード相の内部に、微細なソフト相が分散していることにより、ハード相とソ

フト相が交換結合して、ハード相の保磁力を維持しながら、高い飽和磁化を持つ希土類元素・鉄・ボロン系異方性永久磁石合金を得ることができる。

フロントページの続き

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